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⑤④ **Method for increasing the effect of high-energy explosives mixtures, and explosives mixtures produced in accordance with this method.**

⑤⑦ The present invention relates to a method for increasing the energy conversion from detonating, high-energy, metal-containing explosives mixtures with the aid of exothermic intermetallic alloying reactions between metal components incorporated in the explosives mixture.

The invention also concerns explosives mixtures formulated in accordance with the method.

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The present invention relates to a method for increasing the energy conversion from and thus the effect of detonating, high-energy, metal-containing explosives mixtures by means of specific metal additions, which, in conjunction with explosives incorporated therein being combusted, give rise to exothermic temperature-increasing, intermetallic alloying reactions. These alloying reactions, which are thus initiated by the explosives combustion, continue after the initiation more or less in parallel with the combustion in order to give, as soon as they have got under way, an energy boost to the energy which is released upon the actual explosives combustion. In this way, an increased temperature is obtained, which in turn results in an increased impulse or effect.

The invention also concerns explosives mixtures formulated in accordance with these principles. These principles can also be used for increasing the energy conversion from rocket and ramjet engines. However, this latter area of application has been considered to be so specialised that it is dealt with in another separate patent application filed at the same time as this patent application.

It is previously known that the effect of high-energy explosives mixtures can be considerably increased by means of certain metal additions. However, the enhanced effect obtained in this case can be of different types. Thus, in shaped charges, it is possible to obtain a considerable residual effect by means of the addition of copper and aluminium, whereas, for example, in aluminium-containing underwater charges, it is possible to increase the bubble effect by 25-50 % by means of a suitably adjusted aluminium addition. Aluminium additions are also present in many other mixed explosives. The aluminium addition also gives in fact quite large temperature boosts to the actual combustion reactions. Thus, the high-energy explosive Hexal also includes aluminium powder in addition to the secondary explosive hexogen, and it has been calculated that this addition of aluminium powder, by means of its oxide and carbide formation in conjunction with the combustion of the explosive, gives a temperature boost of about 25 %.

Another alternative for increasing the energy conversion from explosive bodies and rocket propellants, which contain secondary explosives and metal additions, is described in EP-A-0, 323, 828. According to this patent specification, it is possible to increase considerably the energy conversion from those charges known per se, which contain secondary explosives, perchlorates, aluminium powder and binder if, instead of using molar excesses of perchlorate, as was previously the case, the perchlorate portion is balanced against the oxygen balance of the explosives mixture to give an essentially complete formation of carbon dioxide and water.

According to this patent specification, it is in fact the case that previously used excesses of perchlorate

consumed, upon combustion of the charges, far too much energy for the actual break-up in order for the perchlorate addition really to do itself justice. A careful balancing between the perchlorate portion and the oxygen balance of the explosive, would, in contrast, give large quantities of explosive gases, easily reducible with the incorporated metal powder portion, which in turn would give a considerable increase in the effect. There is no reason to doubt this. The greatest disadvantage with this type of explosives mixture is, instead, the perchlorate portion. In practical application it has in fact always been attempted, for reasons of safety, to avoid combinations between perchlorates and high-energy explosives, since the perchlorates as a rule give mixtures which are far too sensitive to handling. In contrast, it is of course customary to use perchlorates in pure pyro charges, which of course only exist in considerably smaller charges than pure explosives mixtures.

However, the present invention now relates to a new and more general method for significantly increasing the piercing capacity and combustion temperature of high-energy explosives mixtures, as well as their bubble effect when they are used in underwater charges. We have in fact found that there are a number of exothermic reactions, comprising one or more metal reactants, which can be combined with explosives combustions and which are started up by these, and which then continue more or less in parallel with these, without any requirement for an energy boost, but instead with release of energy. In addition to the choice of the reactants involved in the exothermic reactions, it is also necessary in this case that these should be available in finely distributed form in intimate contact with each other in the explosives mixture in question. So that the reactants will react exothermically with each other, it is necessary for at least one to be soluble in the other at a given temperature.

The exothermic reaction, where one of the reactants dissolves in the other, is in most cases followed by a second oxide and carbide formation stage, during which the reactants, i.e. in this case the added metals, react with available oxygen and, if appropriate, with carbon incorporated in the explosives molecules. This second stage too is exothermic, but as a rule it is not as powerfully exothermic as stage one.

The oxide and carbide formation stage moreover corresponds in principle to the reaction which is obtained in other metal-containing explosives, for example the Hexal mentioned in the introduction, which only contains hexogen and aluminium, and which is thus completely without other metals with which the aluminium can react exothermically.

Exothermic reactions of particular interest in this connection are those intermetallic alloying reactions which result in borides, aluminides, silicides, alloys

containing alkaline-earth metals and carbides. Since the carbide formation between a metal and carbon from the explosives molecule can here be regarded as taking place according to the same premises as other metallic alloy formations in question here, we consider it justified to include the carbide formation within the definition of intermetallic reactions. Conceivable alternatives in this connection, which we consider to be of particular interest, are the metals titanium, boron, zirconium, nickel, manganese and aluminium, and a reaction between zirconium and carbon included in the explosives molecule. The same also applies to the so-called alkaline-earth metals and hafnium.

So that the intended exothermic intermetallic reactions can be started up by the explosives combustion, it is necessary for the reactants to be accessible and distributed in the explosive in intimate contact with each other and in suitable quantities. When the reactants consist of two or more of the metals mentioned above, this is achieved by producing granules of fine particles, which here means that these are of μ -size, of the reactants and distributing these granules in an explosives matrix which can consist of one or more high-energy explosives such as HMX, RDX, PETN, TATB, NTO, HNS, guanidine derivative such as TAGN, NIGU, and guanidine nitrate or TNT and binder which can be of the energetic binder type, such as polyvinyl nitrate or TNT. (Energetic binder = binder which itself is also an explosive).

Abbreviations used above and in the following, and in this field:

RDX = hexogen
HMX = octogen
HNS = hexanitrostilbene
PETN = pentyl or pentaerythritol tetranitrate
TATB = triaminotrinitrobenzene
NTO = 3-nitro-1,2,4-triazol-5-one
TNT = trinitrotoluene
TAGN = triaminoguanidine nitrate
NIGU = nitroguanidine

In the previously mentioned special case of the invention, where zirconium is made to react with carbon incorporated in the explosives mixture, it is of course also true that the zirconium will be distributed in suitable particle form in the explosives matrix.

As has already been mentioned, the metal reactants for the intermetallic exothermic reaction will be added to the explosives mixture in the form of granules containing fine particles of all the metal reactants (the exception is the carbon in the explosives molecules, which therefore can also be regarded, in terms of function, as a metal in this context), these fine particles of the different metal reactants being as closely connected to one another as possible. These granules can be produced with the aid of small quantities of binder, which can be an explosive (energetic binder) or a binder of another type. Granules produced in another way, without the aid of binders, are also conceivable.

It is previously known that certain intermetallic reactions are exothermic. Other exothermic reactions are also known. The novel aspect of the present invention is, therefore, the combination with explosive, where the explosives combustion is used for the initial energy boost which is required for starting up the exothermic intermetallic reaction, which thereafter contributes a not inconsiderable energy boost to the energy development which is obtained from the explosives combustion. A particular problem in connection with the invention is that of choosing the exothermic reactions which can be used in an explosives context and which give the greatest energy conversion. In addition, it is a matter of choosing metal reactants which in practice can be handled together with explosives and which are economically acceptable with regard to the energy boost which they give. Since the exothermic alloy formations are relatively slow reactions compared to the explosives combustion, the metal admixtures in question here, and the alloying reactions resultant therefrom, involve a certain reduction in the detonation rate of the explosives mixture compared to that of the pure explosive, but at the same time the exothermic metal reaction provides a powerful residual effect in the form of an increased temperature in combination with the formation of liquid/solid particles, which is very favourable when it is a question of creating a powerful piercing effect, for example through steel plate, and when the charge detonates under water and thus gives rise to, among other things, an enhanced bubble effect. In the case of the underwater charge, an extra energy boost is obtained from byproducts which are formed and in turn react with the water which functions as oxidising agent.

Charges of the type characterising the invention are therefore especially well suited for underwater use, i.e. primarily in mines and torpedoes.

The charges according to the invention can be produced as castable PBX (plastic bond explosives) based on metal granules and crystalline explosives and a relatively high binder content. A requirement which must be made of the charges according to the invention is that these must have good cohesion. In those cases where the charges according to the invention are made up of fine-grain binder (1-2 % by weight), granulated crystalline explosive and granules of the metal reactants of the abovementioned type and main binder, one can expect explosives contents in the finished charge of 30-90 % by weight, and alloy metals in quantities of 10-70 % by weight and 1-40 % by weight of binder. The latter can be, for example, a thermosetting resin, a thermoelastic or a thermoplastic such as an acrylate, a

polyurethane, a polyester or a thermoplastic rubber. The lowest binder contents can be obtained if use is made of energetic binders, for example TNT or polyvinyl nitrate, which are both binder and explosive.

The metal and explosives granulates should in our experience have a particle size of 100-200 μm .

One example of an exothermic alloy system applicable in the context of the present invention is $\text{Ti} + \text{B}_2$, which can give an energy boost corresponding to about -71.6 kcal/mol and a reaction temperature of about 4000° K.

Another exothermic system is $\text{Al} + \text{Mn}$.

In contrast, as has already been mentioned, a reaction with pure Al to give aluminium oxide or, if appropriate, aluminium carbide does not increase the energy to the same extent.

A further energy-increasing system is $\text{Zr} + \text{Ni}$.

A corresponding exothermic reaction can also be obtained with zirconium alone, which in this case reacts with carbon from the explosive and can give an energy boost corresponding to -47.0 kcal/mol and a reaction temperature of about 4100° K.

Metal combinations which give exothermic alloy systems and can therefore be appropriate in connection with the present invention

Alkaline-earth metals

Barium plus either bismuth or tin
Magnesium plus tin
Calcium plus aluminium
Strontium plus aluminium
Beryllium plus aluminium

Borides

Boron plus magnesium, carbon, silicon, titanium, zirconium, chromium, molybdenum, tungsten or manganese.

Aluminides

Aluminium plus copper, calcium, boron, titanium or zirconium, chromium, manganese, iron, cobalt, nickel, palladium and platinum.

Carbides

Carbon plus beryllium, calcium, strontium, barium, boron, aluminium.

Silicides

Silicon plus calcium, carbon, titanium, zirconium, hafnium, chromium, molybdenum and nickel.

Furthermore, small additions of substances or alloys from the lanthanide group and/or the metal haf-

nium can be added in order to catalyse the alloying reaction according to the invention.

Production:

The exothermic alloy composition according to the invention is produced expediently by mixing homogeneously the components in question, in suitable particle size, together with a few percent of binder, from which granules of suitable size are produced. We have found that suitable binders for this purpose can be acrylates (solvent-based or water-dispersible). Granules obtained in this way and containing the reactants reacting exothermically upon the explosives combustion are then added to the explosive in question, which can be RDX, HMX, HNS, PETN, or another previously mentioned explosive to give an approximately 10 - 70 % strength mixture.

The metal additions formulated according to the invention can also be used with advantage for castable explosives, for example trinitrotoluene or castable PBX.

A particular advantage of the additions characterising the invention is that these do not cause any appreciable increase in the handling sensitivity of the finished explosives mixtures. This is a very important property, which is not obtained when explosives mixtures are enhanced with pyrotechnic compositions, in which case, on account of their chlorate, perchlorate and/or peroxide contents, a considerable increase in the handling sensitivity of the mixtures must be expected.

The invention which has been defined in the subsequent patent claims will now be illustrated in slightly greater detail with the aid of, on the one hand, a few general examples and, on the other hand, a few more detailed examples.

EXAMPLE 1

Detonating charges

- a) A first explosives mixture consisting of;
 - 60 % RDX (hexogen)
 - 23 % titanium
 - 14 % boron
 - 3 % binder increases the piercing effect by about 20 % compared to a pure RDX composition.
- b) A second explosives mixture consisting of;
 - 68 % RDX (hexogen)
 - 21 % Zirconium
 - 9 % nickel
 - 2 % binder increases the piercing effect by more than 50 % compared to a pure RDX composition.
- c) A third explosives charge consisting of;

50 % RDX (hexogen)
22 % manganese
14 % aluminium
3 % binder

gives an effect which is equivalent to RDX in terms of volume, but the charge density is increased from 1.7 gram/cm³ to 2.4 gram/cm³, which gives an increased effect per unit volume.

EXAMPLE II

Production: Laboratory Scale

Batch IMR-comp 05;

Manganese powder, particle size approximately 10 μ , is mixed with aluminium powder (MIL 512), particle size 2.5 - 5 μ . The mixture is mixed dry, for example in a cube mixer. The composition will be 30 % manganese and 70 % aluminium. The metal composition is mixed with acrylate binder dissolved in trichloroethylene, binder content approximately 1 %. The mixture is dried to approximately 5 - 7 % dry content and is granulated on a 50 mesh sieve-cloth. The granulate is mixed with 50 % RDX, particle size 15 μ , before final drying in a mixer. The explosives composition is finally dried for 12 hours at 60 - 70° C, to a moisture content of <0.1 %.

The batch can thereafter be easily pressed into compacts with a density of 2.35 - 2.40 g/cm³.

In our tests, the composition gave an increased piercing through steel plate, compared with, for example, hexal 70/30.

The test was carried out by placing compacts, with a size of \varnothing 22x20 mm, upright on a steel plate 8 mm thick and with an underlayer of porous wood.

The pellets were initiated using a blasting cap No. 8.

In the test, good piercing results were obtained in all cases, i.e. holes of \varnothing 4-5 mm were formed in the plate. In contrast, corresponding tests with hexal 70/30 result only in the formation of cracks in the plate.

Other mixtures from the various groups gave good results and were produced in principle in accordance with the procedure described above.

Borides

a) Boron and zirconium powder of 0.5-5 μ were mixed in a ratio of 80 % zirconium and 20 % boron, and the mixture was granulated with approximately 1-2 % binder through 50 mesh. The metal mixture was mixed into RDX to a percentage content of 50.

b) Boron and titanium of the same particle size were mixed and granulated in a corresponding manner, with 14 % boron and 23 % titanium, and with addition of 3 % binder. 60 % RDX was then admixed.

The common feature of the two batch recipes described above is that they are converted at a temperature of between 3500 °K and 4200 °K at fully developed pressure.

Claims

1. Method for increasing the energy conversion in the form of piercing capacity, combustion temperature and, in the case of underwater charges, in the form of the bubble effect from detonating explosives mixtures, characterised in that the explosives combustion (detonation) is used to start up an exothermic intermetallic alloying reaction between reactants incorporated in the explosives mixture, after which the said intermetallic alloying reaction continues more or less in parallel with the explosives combustion, without energy boost from the latter, but with the release of energy.
2. Method according to Claim 1, characterised in that metal reactants necessary for the exothermic intermetallic reaction are mixed into the explosives mixture in the form of particles or granules of the order of magnitude of 100-200 μ , each containing all the incorporated metal reactants in the form of particles of μ -size connected to one another.
3. Method according to either of Claims 1 or 2, characterised in that the combustion of the explosive is combined with an exothermic metal reaction in the form of an intermetallic alloying reaction comprising two or more metals which, as final product, are given a boride, an aluminide, a silicide, an alloy of alkaline-earth metals or, alternatively, a carbide.
4. Method according to any one of Claims 1 - 3, characterised in that the combustion of the explosive is combined with an exothermic metal reaction in the form of either an intermetallic alloying reaction between two or more of the metals titanium, boron, zirconium, nickel, manganese and aluminium, or alternatively between zirconium and carbon incorporated in the explosive.
5. Method according to any one of Claims 1-4, characterised in that the mixture ratio between the incorporated components is chosen within the following ranges
 - 10-70 % by weight of alloy metal
 - 30-90 % by weight of explosive, and
 - 1-40 % by weight of binder.
6. Method according to any one of Claims 1-5,

characterised in that the alloy metals are distributed in an explosives binder matrix in the form of granules with a particle size of 100-200 μm .

7. High-energy explosives mixture produced in accordance with the method according to any one of Claims 1-6, characterised in that there is also incorporated therein, in addition to an appropriate binder, which can be energetic, and one or more secondary explosives of the type RDX, HMX, HNS, PETN, TATB, NTO, HNS, guanidine derivative, such as TAGN, NIGU, guanidine nitrate or trinitrotoluene, a metal addition which, upon combustion of the secondary explosive, gives rise to an exothermic intermetallic alloying reaction.

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8. High-energy explosives mixture, characterised in that the metal addition includes at least two metals which, in the intermetallic alloying reaction, give a boride, an aluminide, a silicide, an alloy of alkaline-earth metals or a carbide.

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9. High-energy explosives mixture according to Claim 8, characterised in that it includes therein at least two of the metals titanium, boron, zirconium, nickel, manganese or aluminium.

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10. High-energy explosives mixture according to Claim 8, characterised in that the metal addition consists of zirconium.

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11. High-energy explosives mixture according to any one of Claims 7-10, characterised in that the metal addition is incorporated in the form of granules or particles consisting of all the incorporated metals in the form of particles of μ -size connected to a binder which can be energetic, the granules having a size of 100-200 μm and being distributed in the explosives matrix which can also contain binders of the same or another type.

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12. High-energy explosives mixture according to one or more of Claims 7-11, characterised in that it comprises

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30-90 % by weight of explosive

10-70 % by weight of alloy-forming metal,

and

1-40 % by weight of binder.

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**European Patent
Office**

EUROPEAN SEARCH REPORT

Application Number

EP 91 85 0269

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X A	US-A-4 331 080 (M.M. WEST ET AL) * column 1, line 42 - column 12, line 30; claims 1-28 *	1,3-5, 7-10 2,6,11, 12	C06B45/10 C06B33/10
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C06B C06C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 FEBRUARY 1992	Examiner BLASBAND I.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document	